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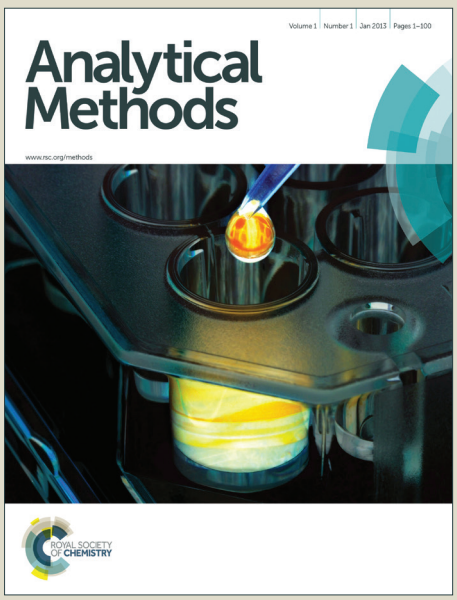

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Rapid Determination of Sulfide Sulfur in Anaerobic System by Gas-phase Molecular Absorption Spectrometry

Dong Chen, Shilei Li, Haibo Liu, Tianhu Chen*, Chen Chen, Chao Yu
Laboratory for Nanomineralogy and Environmental Material, School of Resource and Environmental Engineering, Hefei University of Technology, China

Abstract

Sulfide sulfur is an important indicator of environmental monitoring and anaerobic bioengineering, has attracted increasing attention due to its significance in the anaerobic biotreatment process and high toxicity to human and aquatic microorganisms. A detection system was designed for rapid and accurate determination of sulfide sulfur in anaerobic system by gas-phase molecular absorption spectrometry (GPMAS). Based on the maximum absorption of hydrogen sulfide (H_2S) at 202.6 nm, the calibration curve between sulfide content and absorbance was obtained, which was used to calculate the sulfide concentration in samples. The simulated samples of landfill leachate were detected after anaerobic reaction. A new method for removal of the effects of interference ions on determination of sulfide in the fermentation broth was proposed. The results showed that the method gave satisfactory precision and recovery. The detection limit of H_2S in biogas is 5.1×10^{-3} mg L^{-1}, the quantification limit is 1.7×10^{-2} mg L^{-1}; the detection limit of S^{2-} in fermentation broth is 1.2×10^{-2} mg L^{-1}, the quantification limit is 4.1×10^{-2} mg L^{-1} while the detection limit of acid volatile sulfide (AVS) in fermentation residue is 2.7×10^{-2} mg g^{-1}(dry sample) and the quantification limit is 8.9×10^{-2} mg g^{-1}(dry sample). This indicates that the proposed method is suitable for determination of sulfide sulfur derived from anaerobic system.

Keywords

Sulfide sulfur; Anaerobic system; Landfill leachate; Gas-phase molecular absorption spectrometry; Acid volatile sulfide

Introduction

The rapid development of social economy and industrialization resulted in serious energy and environmental issues. The anaerobic fermentation has been used to dispose waste and recycle

* Author to whom should be addressed. Tel.: +86 13956099615, +86 0551 62903990.
E-mail address: chentianhu@hfut.edu.cn; chentianhu168@vip.sina.com

energy by producing methane which is a kind of high-quality and clean energy[1]. Organic sulfur compounds and inorganic sulfates are biodegraded into sulfide sulfur in anaerobic system. The distribution of sulfide sulfur in biogas, fermentation broth, and fermentation residue varies with pH, alkalinity, content of transition metal elements, and temperature of anaerobic system[2,3]. H_2S in biogas results in the decrease of the quality of the biogas and causes corrosion in pipes. In addition，the combustion of biogas containing H_2S produces secondary pollutant of SO_2. A high concentration of sulfide in fermentation broth affects the process of anaerobic fermentation by inhibiting the activity of methane bacteria[4]. Therefore, developing a rapid and accurate method for detection of sulfide sulfur in biogas, fermentation broth, and fermentation residue plays crucial role in research of biochemistry process[5], interaction between micro-organisms and soil minerals[6,7], as well as management of energy recovery system of anaerobic fermentation of organic waste[8,9].

Currently, a lot of methods are carried out to detect sulfide sulfur, such as spectrophotometry, iodometry, fluorescence, ion chromatography, etc. Spectrophotometry is one of the classic sulfide determination methods. The earliest and best known spectrophotometry is the colorimetric methylene blue method developed by Johnson and Nishita. Under suitable conditions, the sulfide solution reacts with p-aminodimethylaniline in the presence of Fe^{3+} to develop a dark blue colour[10]. The intensity of the blue colour is significantly influenced by temperature and strong reducing agents. Besides, the volatility and instability of sulfide make the accuracy of the determination lower. Sulfide determination can also be achieved by iodometry[11], but the method has many disadvantages. Under acid condition, sulfide is oxidized by excess iodine. Afterwards, the surplus iodine is titrated by sodium thiosulfate standard solution. The concentration of sulfide is obtained indirectly in this way. Therefore, the iodometry involves many titration processes in which many reagents are used and test time increased. Practically, the repeatability of the iodometry is poor because of the instability of sulfide and long detection time. Fluorescence generally has higher sensitivity. Petruci et al develop a new palladium chelate compound is described for the determination of sulfide in aqueous samples[12]. Also, the accuracy of fluorescence is seriously affected by the volatility and instability of sulfide. More interference factors and reagents used make the method complex and hard to operate. The multiple ions can be simultaneously determined by ion chromatography, but significant disadvantages restrict the application of ion chromatography in determination of sulfide, for example, the chromatographic column is easily blocked and the samples need to be cleaned. The reducibility of sulfide in anaerobic system is stronger than that in natural water resource. The former is more volatile and easily oxidized in air and should be detected in a short period of time even through sulfide antioxidant buffer solution plays a certain role. Therefore, the above methods cannot effectively or conveniently detect sulfide sulfur in anaerobic system.

GPMAS was first proposed by Cresser in the 1970s[13-15], which was based on upgrading reform of atomic absorption instrument. In the past decades, some scholars had been dedicating to upgrade the structure of the instrument, optimize the conditions of determination and study effects of different interference ions. Syty replaced the flame of an atomic absorption spectrophotometer with a flow-through absorption cell. A convenient reaction vessel was used for gas-liquid separating[16]. Cresser described an automated method for the determination of sulfide in solution that involved the interfacing of automatic sampler, a proportioning pump and a gas-liquid separator to an atomic absorption spectrometer[17]. Meanwhile, optimization of experimental conditions was studied in their works. A wavelength of 200 nm was employed for optimum sensitivity. There was no significant improvement at different temperatures. Therefore, their studies were carried out at room temperature. In interference experiments, Nitrite and sulfite showed pronounced interference in determination of sulfide. Afterwards, GPMAS was applied to determination of sulfide in waste water using a fully automated system[18]. However, their works were only focus on the determination of sulfide sulfur in solution. No effective method for eliminating the effects of different interference ions was put forward. In the present work, it was found that GPMAS could be applied to simultaneously detect concentration of H_2S in biogas, S^{2-} in fermentation broth and AVS in fermentation residue. At the same time, a new method based on the application of Cu^{2+} to precipitate S^{2-} was proposed to eliminate the effects of interference ions on determination of sulfide in fermentation broth. Compared with other detection methods, the determination of sulfide by GPMAS offers many advantages, such as short detection time, wide range of concentrations determined, strong anti-jamming performance, no complex chemical separation. Therefore, GPMAS is suggested as a kind of effective analysis method for determination of sulfide sulfur in anaerobic system. The feasibility and detection limit of GPMAS for determination of sulfide sulfur were performed in the present work.

Detection system

Principal

For specific wavelength of light passing through the spectrometer, the intensity of the light passing through the absorption cell is measured. The variation of light intensity obeys Beer-Lambert's law. H_2S is swept into the absorption cell in the light path of gas-phase molecular absorption spectrometer. The absorbance at 202.6 nm is measured using a hollow-cathode lamp.

$$I(\lambda)=I_0(\lambda)\exp[-Lc_{H_2S}\alpha_{H_2S}(\lambda)] \quad (1)$$

According to formula (1), the concentration of H_2S is calculated from the followed formula:

$$c_{H_2S}(g)=\frac{1}{\alpha_{H_2S}(\lambda)L}\ln\left|I_0(\lambda)/I(\lambda)\right| \quad (2)$$

Absorbance (A) is the negative logarithm of transmittance (T), indicating the extent that the incident light is absorbed.

$$T=I(\lambda)/I_0(\lambda) \quad (3)$$

$$A=-\ln T=\ln\left|I_0(\lambda)/I(\lambda)\right| \quad (4)$$

Therefore，formula (2) can be transformed into formula (5)：

$$c_{H_2S}(g)=\frac{1}{\alpha_{H_2S}(\lambda)L}A \quad (5)$$

where, λ denotes the characteristic wavelength of H_2S in ultra violet. I_0 (λ) represents the intensity of incident light at the wavelength of λ. I (λ) represents the intensity of emergent light. $\alpha_{H_2S}(\lambda)$ is molar absorptivity. $c_{H_2S}(g)$ is the concentration of H_2S. L is the length of absorption cell.

As seen from the formula (5), the absorbance (A) has a linear relationship with the concentration of H_2S.

Structure of instrument

Structure of gas-phase molecular absorption spectrometer is shown in Fig. 1. A fixed-wavelength zinc lamp is used to provide light at the analytical wavelength of 202.6 nm. Air serves as carrier gas. The air flow rate which is regulated by a flow meter is 0.5 L min^{-1}. H_2S is swept by the carrier gas into the absorption cell and absorbed by activated carbon which is used for off-gas treatment. The intensity of the light passing through the absorption cell is measured, and the final determination results are shown in the form of absorbance.

Experimental

Instrument and accessories

(1) AJ-2100 gas-phase molecular absorption spectrometer (An Jie Environmental Technology Co., Ltd. Shanghai, China);

(2) Head space bottles, 124.5±0.5 mL, with silicone rubber plugs and plastic bottle caps;

(3) Anaerobic reaction bottles, 300 mL, with silicone rubber plugs and aluminous bottle caps;

(4) 1mL and 250μL Gas Syringes (SGE Analytical Science Company, Australia);

(5) Gauze, nine layers.

Reagents

All the chemical reagents used in the experiments were purchased from chemical reagent company without further purification. CH_4 (99.999%); CO_2 (99.99%); N_2 (99.99%); NH_3 (0.5% NH_3+99.5%Ar); H_2S standard gas (3% H_2S +97%N_2); H_2 (99.999%); ZnS (≥95%); HCl solution (6mol L^{-1}); Landfill leachate (From Longquan Mountain landfill, Feidong, China)

Sufide antioxidant buffer (SAOB) was prepared from 0.5 mol L^{-1} sodium hydroxide, 0.05 mol L^{-1} L-ascorbic acid and 0.05 mol L^{-1} sodium citrate. Sulfide stock standard solution was prepared by weighing 0.7g $Na_2S{\cdot}9H_2O$ on an analytical balance and dissolving to 100mL in the SAOB solution.Working standards were freshly prepared each day in the SAOB solution by the least number of dilution steps possible and detected by iodimetrc titration. A 14.70 mg·S^{2-} L^{-1} working standard solution was obtained by the above method.

Various solutions of cations and anions for the interference studies were prepared at levels of 500 mg L^{-1} and 1000 mg L^{-1} using analytical-reagent grade salts. The solutions were prepared in ultrapure water (Millipore MilliQ, 18.2 MΩ cm) in the experiments.

Parameters of instrument

Electric current: 5mA; Wavelength: 202.6 nm; Determination mode: Peak height; Determination time: 20 s; Carrier gas (air) flow rate: 0.5 L min^{-1}

Simulation experiment

Landfill leachate was collected from Longquan Mountain landfill. The characteristics of the landfill leachate were represented by the basic parameters: COD 11388 mg L^{-1}, TOC 2507 mg L^{-1}, pH 7.49, ammonium nitrogen 650 mg L^{-1}, total phosphorus 0.29 mg L^{-1}.

Five groups of samples were prepared by adding landfill leachate to 250 mL of anaerobic reaction bottles containing 20g of anaerobic sludge. Nitrogen (N_2) was filled into the reaction bottles in order to replace the air and keep anaerobic condition. The five groups of parallel samples were labelled as A, B, C, D and E, and cultured in a constant temperature incubator at 35 ^{o}C for 1 month.

Results and discussion

Choice of carrier gas

The effect of the choice of carrier gas on determination of sulfide sulfur was investigated by nitrogen and air, but no significant difference was observed. All of the data in this study were collected by carrier gas of air.

Choice of carrier gas flow rate and test time

The influence of air flow rate on the absorption signal was evaluated by making a series of analyses of 200 μL of the H_2S standard gas and 0.5 mL of 43.8 μg mL^{-1} S^{2-} while varying the

flow rate from 0.2 to 1.0 L min^{-1}. The results are presented in Table 1. The results indicate that the sulfide absorption intensity gradually decreased with increasing flow rate. Clearly the highest absorbance signals were observed at low flow rates. This is because the dilution of the evolved H_2S by the carrier gas was less. However, peak time increased with decreasing air flow rate and a lower air flow rate gave rise to very broad peaks, namely test time was increased. Therefore, a convenient flow rate of 0.5 L min^{-1} and test time of 20 s were selected for further work.

Choice of acid volume and concentration

The effect upon the evolution of H_2S of changing the volume and the concentration of HCl added to the gas-liquid separator was tested and some of the data are presented in Table 2 .As Table 2 shows, while keeping acid concentration constant, the increasing volume of acid injected into the gas-liquid separator had a slight decrease in signal intensity. This might be due to the concentration of S^{2-} was diluted by the acid injected. As expected, further increases in concentration of acid gave rise in signal intensity. It is mainly because higher concentration of acid enhance chemistry reaction and improve the speed of evolution of H_2S. Obviously a excess of the acid is adequately towards complete evolution of H_2S. Therefore, 2.5 mL of 6 mol L^{-1} HCl solution was used in the present experiment on determination of sulfide in solution.

Effect of reaction time on detection of AVS

Reaction time is an important parameter that influences the extraction efficiency and repeatability of GPMAS. In order to establish the optimal reaction time of AVS determination, the experiments of reaction time were operated by adding 6mol L^{-1} HCl solution into the headspace bottles containing 5g of the fermentation residue. The samples were heated in 100℃ water bath. The results, shown in Fig. 2, indicate that the measured AVS increased rapidly in 40 min, then experienced a slight increase from 40 to 50 min, after that no distinct increase was observed (up to at least 2 h). Therefore, it is suggested that the reaction time for determination of AVS should be at least 1h.

Determination of the concentration of H_2S in the biogas

Calibration curve of H_2S determination. Sandard gas of H_2S was collected by a gas bag made of aluminium foil. Afterwards, 0, 50, 100, 150, 200 and 250μL of H_2S were respectively injected into the gas-liquid separator in the gas path of gas-phase molecular absorption spectrometer. The gas was carried into the absorption cell by air and the absorbance was measured by GPMAS. The relationship between the mass of H_2S (X, μg) and the absorbance (A) was established as a calibration curve. The regression equation of the calibration curve was obtained as followed: $A = 0.0116 X + 0.0012$, $R= 0.9997$.

Detection limit and quantification limit of H_2S determination. Replicate analyses (n=10) of the blank composed of air gave a standard deviation of 9.832×10^{-5}. Defining the detection limit

as the concentration of sulfide which yields a signal of three times the standard deviation of the blank. The quantification limit is defined as the concentration of sulfide which yields a signal of ten times standard deviation of the blank[19]. The lower limit of detectability (LLOD) and the limit of detection (LOD) are calculated based on the standard deviation of the blank absorbance (SD) and the slope of the calibration curve (S) according to the formula:

$$LLOD = 3SD/S \quad (6)$$

$$LOD=LLOD/V=3SD/(SV) \quad (7)$$

where, V is maximum volume of injection.

Limit of quantification (LOQ) is calculated according to the followed formula:

$$LOQ = 10SD/(SV) \quad (8)$$

The results are summarized in Table 3.

Interference of different gases. To the best of our knowledge, the anaerobic reaction produces a biogas, consisting of CH_4, CO_2, H_2O, H_2S, NH_3, N_2, etc. Therefore, the effects of the interference gases were investigated by measuring the intensity of light at 202.6 nm after injection of the different gases in this work. As displayed in Table 4, just tiny change of the absorbance at 202.6nm is observed, which can be omitted compared with the absorbance of H_2S. In other word, the determination of H_2S almost does not be interfered by the extra gases. Therefore, the proposed method for determination of H_2S in anaerobic system is feasible in this aspect.

Precision and recovery of H_2S determination. After 1 month, the anaerobic bottles were taken out from constant temperature incubator. Instantly, 2 mL of the gases in the anaerobic samples was injected into the gas path of gas-phase molecular absorption spectrometer. The results of H_2S concentration were measured and displayed in Table 5. As presented in Table 5, the relative standard deviation of the replicate measurements (n=10) is lower than 2%.

The recovery experiments were carried out by mixing 1mL of the gas in the five samples with 2.28μg of the standard gas of H_2S (50μL). The absorbance of the mixtures were measured by GPMAS. Afterwards, the recovery was calculated according to the mass of intially present H_2S in the samples, H_2S added and H_2S found. The recovery varied between 95% and 102% as presented in Table 5.

Determination of the concentration of sulfide (S^{2-}) in the fermentation broth

Calibration curve of S^{2-}. Respectively, 0.00, 0.50, 1.00, 1.50, 2.00, and 2.50 mL of working standard solution (14.70 mg·S^{2-} L^{-1}) were injected into the gas-liquid separator followed by adding ultrapure water to 5 mL. Afterwards, 2.5 mL of hydrochloric acid (6 mol L^{-1}) was added with a quantitative liquid filling device. The gaseous product was stripped from the solution by a stream of air and introduced into the absorption cell, where its absorbance was measured at 202.6nm. The

regression equation of the calibration curve was obtained as followed: A = 0.0074 X + 0.0023, R= 0.9994, where, X is the mass of S^{2-} in μg.

Detection limit and quantification limit of S^{2-} determination. The calculation method of detection limit and quantification limit of sulfide in fermentation broth is identical with detection limit and quantification limit of H_2S as described above. The blank composed of 1mL of SOAB solution and 2.5 mL of hydrochloric acid was measured ten times. The detection limit and quantification limit of S^{2-} are presented in Table 3.

Interference of different ions（32.0μg S^{2-}/0.5mL）. The effects of interference ions Ni^{2+}, Zn^{2+}, Ca^{2+}, Mg^{2+}, Mn^{2+}, Co^{2+}, Fe^{2+}, Ag^{+}, Cu^{2+}, NO_2^-, CO_2^{2-}, SO_4^{2-}, SO_3^{2-} and $S_2O_3^{2-}$ were investigated by adding the ions into the solution. The determination results after adding the ions into a 32μg S^{2-} /0.5mL of fermentation broth are presented in Table 6. As shown in Table 6, almost no effect on determination of S^{2-} was observed when Ni^{2+}, Zn^{2+}, Ca^{2+}, Mg^{2+}, Mn^{2+}, Fe^{2+} and SO_4^{2-} was added into the solution at levels of 500 mg L^{-1} and 1000 mg L^{-1}. However, Co^{2+} had slight interference on detection while Ag^{+} and Cu^{2+} had severe effects on the analysis because they formed extremely insoluble sulfides with S^{2-}. NO_2^-, SO_3^{2-} and $S_2O_3^{2-}$ markedly affected the determination of S^{2-} due to the produced gases had certain absorption of the light at 202.6 nm. Therefore, Ag^{+}, Cu^{2+}, NO_2^-, SO_3^{2-} and $S_2O_3^{2-}$ significantly interfered determination of S^{2-}.

At the same time, other scholars had also observed the deleterious effect of Cu^{2+} on the determination of S^{2-}[16,18]. In their studies, the relative error of Cu^{2+} on the determination of S^{2-} was about -100%, which was identical with the result of adding excess Cu^{2+} into a working standard solution of S^{2-}. However, -93.4% of relative error is displayed in the determination of the fermentation broth (see Table 6). This is because the gases produced from the different interference ions cause absorption signal when S^{2-} forms insoluble compounds with excess Cu^{2+}. The result implies that the effects of the interference ions described above on determination of S^{2-} in fermentation broth can be eliminated by addition of excess Cu^{2+}. The concentration of S^{2-} is calculated according to the followed formula:

$$c_{(S^{2-})} = c_{(M)} - c_{(P)} \quad (9)$$

where, $c_{(S^{2-})}$ is the actual concentration of S^{2-}, $c_{(M)}$ and $c_{(P)}$ are the concentration of S^{2-} before and after addition of excess Cu^{2+}.

Precision and recovery of S^{2-} determination. The fermentation broth was diluted in the SAOB solution because the concentration of sulfide is much higher than the maximum detectable concentration of GPMAS. In the present work, 0.5 mL of sample was injected. The absorbances of five samples before and after addition of excess Cu^{2+} were respectively measured ten times by the proposed method. The results were obtained by calculating based on the formula (9) and shown in

Table 7.

The recovery experiments were conducted with the 0.5mL of fermentation broths diluted 10 times, standard addition was 0.5 mL of S^{2-} (14.7 mg L^{-1}). The recovery was calculated according to the mass of initially present S^{2-} in the samples, S^{2-} added and S^{2-} found. The recovery varied between 88% and 112% and summarized in Table 7.

Determination of the acid volatile sulfide (AVS) in fermentation residue

AVS is operationally defined as the amount of sulfides volatilized by the addition of hydrochloric acid [20] and mainly composed of iron and manganese sulfides. AVS is active sulfur in fermentation residue. However, AVS cannot completely be extracted from the fermentation residue within the longest test time of gas-phase molecular absorption spectrometer, because the reaction between AVS and hydrochloric acid is slow and not sufficient. In order to increase the reaction time and make AVS escape from the fermentation residue sufficiently, headspace analysis [21] and water bath were used for determination of AVS. The samples were added into the headspace bottles, in which the air was replaced by nitrogen for keeping the reaction oxygen-free. The relationship between AVS in the fermentation residue and absorbance is established based on the concentration of H_2S in the headspace bottles.

Calibration curve of AVS. The purity of ZnS used in this experiment, measured by iodimetrc titration, comes to 96.66%. The measured ZnS serves as the standard reagent of AVS determination. 0.00 g, 0.01 g, 0.02 g , 0.03 g, 0.04 g and 0.05 g of ZnS were added into the headspace bottles. The air in the headspace bottles was replaced by nitrogen. The headspace bottles were sealed and heated in the water bath at 100^{o}C for 1h after adding 10 mL of 6 mol L^{-1} HCl solution. The bottles were taken out after the reaction is completed, namely most of the AVS transferring into hydrogen sulfide. 200 μL of gas in headspace bottles was injected into the gas-liquid separator and swept by carrier gas into the absorption cell. The absorbance (A) was measured by GPMAS. Calibration curve between AVS and absorbance was obtained as followed: A=0.0195X+0.0021, R=0.9995, where, X presents the mass of AVS in mg.

Detection limit and quantification limit of AVS determination. The blank prepared by adding 10 mL of hydrochloric acid (6 mol L^{-1}) to headspace bottle was measured ten times. The recorded absorbance had a standard deviation of 1.049×10^{-4} .The calculation method of detection limit and quantification limit of AVS determination in fermentation residue is fundamentally identical with the above. Detection limit and quantification limit of AVS were calculated as folllowed formula:

$$LOD=LLOD/M=3SD/(SM) \quad (10)$$

$$LOQ = 10SD/(SM) \quad (11)$$

where, V in the original formula is replaced by maximum mass of fermentation residue (M). The results are summarized in Table 3.

Precision and recovery of AVS determination. In this section, the fermentation residue in anaerobic bottles was filtered with gauze. 5g of the fermentation residue (wet) was added into the head space bottles. The results were obtained by the procedure described above. The rest of fermentation residue was dried in an oven at 100 ^{o}C for 24h to obtain the moisture content of the sample reaching 87.85%. Thus, AVS of fermentation residue is calculated and summarized in Table 8.

The recovery experiments were carried out with 0.03g of pyrrhotite, sphalerite and ferrous sulfide, replacing the fermentation residue due to the low content of AVS in the fermentation residue. Standard addition of AVS is 10 mg. The recovery was calculated according to the mass of intially present AVS in the three minerals, AVS added and AVS found. The results are shown in Table 9.

Conclusions

In the present work, a more convenient, feasible and scientific method was exploited to determine various forms of sulfide sulfur including biogas, fermentation broth and fermentation residue derived from anaerobic system using GPMAS. The simulation experiments were operated with five groups of anaerobic reaction, in which the landfill leachate was used to be the source of carbon and sulfur. The simulation samples of landfill leachate were detected after anaerobic reaction, the relative standard deviation of repeated measurements was lower than 2%. The concentration of the sulfide sulfur in the anaerobic system was higher than the detection limit of the proposed method. Furthermore, a new method based on the application of Cu^{2+} to precipitate S^{2-} was proposed to eliminate the effects of interference ions on determination of sulfide in fermentation broth. The results showed that a good precision and appreciated recovery values were obtained. In summary, the system shows high efficiency in detection of sulfide sulfur in anaerobic system besides its advantages of resisting the disturbance from environmental factors and rapid testing.

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Table and Figure captions

Table 1 Choice of carrier gas flow rate and test time

Air flow rate ($L\ min^{-1}$)	Gas (H_2S)			Solution (sulfide)		
	Test time (s)	Peak time (s)	Peak height (absorbance)	Test time (s)	Peak time (s)	Peak height (absorbance)
0.2	20	18.2	0.1266	30	20.4	0.1764
0.5	10	8	0.1089	20	11.8	0.1643
0.8	10	6	0.0956	10	8.3	0.1532
1.0	10	5.5	0.0950	10	6.8	0.1482

Table 2 Choice of acid volume and concentration

Volume of acid (mL)	Peak height (Absorbance)			
	6.0 mol L^{-1} HCl	4.0 mol L^{-1} HCl	2.0 mol L^{-1} HCl	1.0 mol L^{-1} HCl
1	0.1669	0.1583	0.1505	0.1351
2	0.1643	0.1492	0.1386	0.1299
3	0.1568	0.1382	0.1268	0.1213
4	0.1457	0.1368	0.1201	0.1186

Table 3 Limit of detection and limit of quantification

Parameter	Value		
	Gas (H_2S)	Liquid (Na_2S)	Solid (AVS)
Standard deviation (n=10)	9.832×10^{-5}	7.528×10^{-5}	1.049×10^{-4}
Calibration curve	A = 0.0116 X + 0.0012	A = 0.0074 X + 0.0023	A=0.0195X+0.0021
Correlation coefficient	0.9997	0.9994	0.9995
Maximum volume or mass of injection	5 mL	2.5 mL	5 g (The mass of dry sample is 0.6075g)
Limit of detection	5.1×10^{-3} mg L^{-1}	1.2×10^{-2} mg L^{-1}	2.7×10^{-2}mg g^{-1}(dry sample)
Limit of quantification	1.7×10^{-2} mg L^{-1}	4.1×10^{-2} mg L^{-1}	8.9×10^{-2}mg g^{-1}(dry sample)

Table 4 Interference of different gases

Interference	Volume of injection (mL)	Absorbance	Interference	Volume of injection (mL)	Absorbance
CH_4	0.2	0.0004	NH_3	0.2	0.0003
	1.0	0.0003		1.0	0.0002
	5.0	0.0004		5.0	0.0002
CO_2	0.2	0.0003	N_2	0.2	0.0002
	1.0	0.0004		1.0	0.0005
	5.0	0.0003		5.0	0.0003
H_2	0.2	0.0003	H_2O (liquid)	1.0	0.0002
	1.0	0.0002			
	5.0	0.0004			

where, a part of H_2O (liquid) will transfer into water vapor under the action of carrier gas.

Table 5 Precision and recovery of H_2S determination

Sample	Concentration of H_2S (n=10, mg L^{-1})	RSD (%)	H_2S initially present (μg)	H_2S added (μg)	H_2S found (μg)	Recovery (%)
A	1.76±0.04	1.82	1.76	2.28	3.99	97.81
B	2.00±0.03	1.30	2.00	2.28	4.22	97.37
C	2.23±0.06	1.75	2.23	2.28	4.40	95.18
D	1.44±0.05	1.95	1.44	2.28	3.76	101.75
E	2.01±0.06	1.73	2.04	2.28	4.32	100.00

where, RSD (%) is the relative standard deviation.

Table 6 Interference of different ions (32μg S^{2-} /0.5mL)

Interferent	Interferent level (μg)	Measured value (μg)	Relative error (%)	Interferent	Interferent level (μg)	Measured value (μg)	Relative error (%)
Ni^{2+}	500	32.6	+1.9	Ag^{+}	500	5.4	-83.2
	1000	32.2	+0.6				
Zn^{2+}	500	31.7	-0.9	Cu^{2+}	500	2.1	-93.4
	1000	32.2	+0.6				
Ca^{2+}	500	32.4	+1.3	NO_2^{-}	500	67.8	+111.9
	1000	32.3	+0.9				
Mg^{2+}	500	31.5	+1.6	CO_3^{2-}	500	33.0	3.1
	1000	32.3	+0.9		1000	30.9	-3.4
Mn^{2+}	500	32.0	0	SO_4^{2-}	500	32.1	+0.3
	1000	32.4	+1.3		1000	32.0	0
Co^{2+}	500	31.0	-3.1	SO_3^{2-}	500	77.6	+142.5
	1000	30.2	-5.6				
Fe^{2+}	500	32.2	+0.6	$S_2O_3^{2-}$	500	33.1	+3.4
	1000	32.4	+1.3		1000	38.6	+20.6

Table 7 Precision and recovery of S^{2-} determination

Sample	$c_{(M)}$ (mg L^{-1})	RSD (%)	$c_{(P)}$ (mg L^{-1})	RSD (%)	$c_{(S^{2-})}$ (mg L^{-1})	S^{2-} (μg)			Recovery (%)
						Initially present	Added	Found	
A	141.77±2.53	1.93	9.28±0.10	0.63	132.49	6.62	7.35	14.03	100.82
B	181.04±2.39	1.00	12.37±0.12	0.71	168.67	8.43	7.35	16.59	111.02
C	145.09±2.12	1.32	8.17±0.09	0.74	136.92	6.85	7.35	14.87	109.12
D	153.15±3.61	1.92	8.81±0.17	1.10	144.34	7.22	7.35	13.75	88.84
E	174.10±3.02	1.38	9.09±0.06	0.42	165.01	8.25	7.35	16.13	107.21

Table 8 Precision of AVS determination

Sample	AVS (n=10, mg g^{-1}(dry sample))	RSD (%)
A	3.98±0.05	1.47
B	4.22±0.06	1.00
C	3.97±0.09	1.34
D	4.08±0.07	1.16
E	4.05±0.05	0.60

Table 9 Recovery of AVS determination

Sample	AVS initially present (mg)	AVS added (mg)	AVS found (mg)	Recovery (%)
Pyrrhotite	7.47	10.00	17.73	102.60
Sphalerite	7.11	10.00	17.20	100.90
Ferrous sulfide	8.79	10.00	18.54	97.50

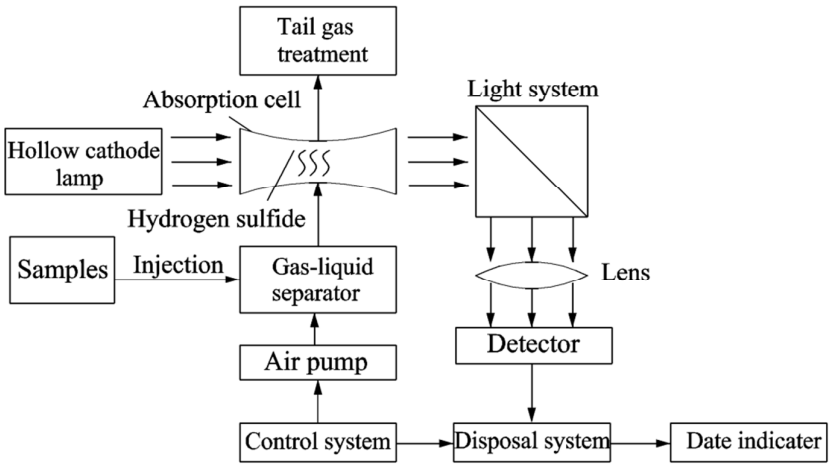

Fig. 1 Schematic diagram of gas-phase molecular absorption spectrometer

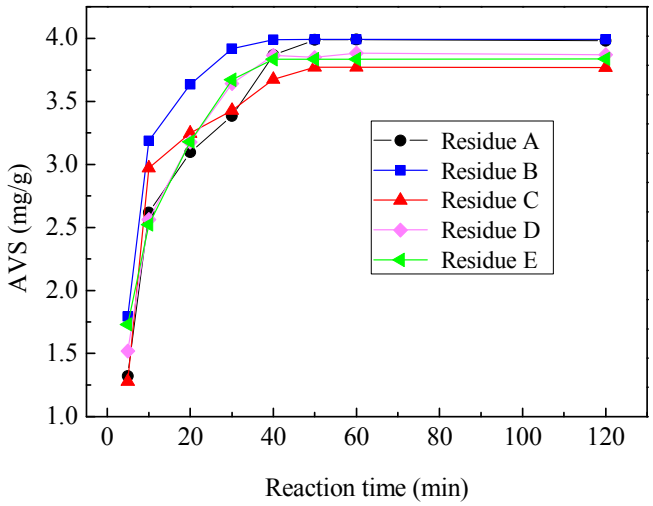

Fig. 2 Effect of reaction time on detection of AVS